
(12) UK Patent Application (19) GB (11) 2 111 484 A

(21) Application No 8231143

(22) Date of filing 1 Nov 1982

(30) Priority data

(31) 317207

(32) 2 Nov 1981

(33) United States of America (US)

(43) Application published 6 Jul 1983

(51) INT CL³
C07C 69/73 C08F 2/26 //
20/00

(52) Domestic classification
C2C 200 20Y 220 227

22Y 233 240 30Y 364 366

367 368 36Y 491 638 644

652 658 65X 662 806

80Y 814 AA BZ CW

C3P JB

C3W 225

U1S 1346 1349 1368

3016 3023 C2C C3P

(56) Documents cited

GB 1535278

GB 1533392

GB 1490673

(58) Field of search

C2C

(71) Applicant

The Kendall Company
(USA—Delaware),
One Federal Street,
Boston, Massachusetts
02110, United States of
America

(72) Inventor

Edward Witt

(74) Agent and/or Address for

Service
Kilburn and Strode,
30, John Street, London,
WC1N 2DD

**(54) Unsaturated monoester
emulsion polymerization stabilizers**

(57) Stabilizers for the emulsion
polymerization of olefinic monomer
and comonomer systems comprise
the half esters of non-ionic
ethoxylates of formula



in which R is C₈₋₃₀ linear alkyl or C₄₋₁₈
mono-, di- or tri-alkyl phenyl and R is
linked to ethoxy by O, S or N and x is
4—10 with α,β-ethylenically-
unsaturated dicarboxylic acids,
preferably maleic, citraconic, and
itaconic acids. Stable, low floc, latices
having good shear are obtained useful
as pressure and non-pressure
sensitive adhesives. The olefinic
unsaturated monomers are those of
the vinyl and acrylic types.

GB 2 111 484 A

SPECIFICATION

Emulsion polymerization stabilizers

The present invention relates to stabilizer compounds and their use in the emulsion polymerization of olefinic monomers generally to form stable, low floc latices and particularly to such latices having utility as industrial pressure and non-pressure sensitive adhesives. 5

The use of surfactants in emulsion polymerization proves less than satisfactory due to the migratory nature of the surfactant as well as water sensitivity imparted by such surfactant to the polymer product. Proposed emulsion stabilizer systems include compounds of the monomeric type, i.e. having at least one olefinic bond and capable of undergoing copolymerization with the primary polymer. 10

10 forming monomer thereby becoming incorporated into the main polymer chain. Stabilizers of the type described e.g. in U.S. Patent 4,029,658, 3,893,166, 3,925,442 and 3,483,155 must usually be employed in a polymerization system substantially devoid of electrolyte to avoid flocculation and coagulum formation. This generally precludes the use of polymerization catalysts which often provide more favourable polymerization rates and polymer structures. 15

15 Many latices suitable for adhesive use must be resistant to high temperature and humidity and thus stability and water sensitivity characteristics are of primary importance. Water vapour transmission rate (WVTR) which measures the capacity of the adhesive to pass or transmit moisture is likewise relevant to the question of adhesive bond permanency in moist environments. It is further desirable that the polymerization process permits high conversion of monomer (at least 80 and preferably 90% and above) to polymeric form. Stabilizers thus far proposed for the aforescribed use are found to be less than adequate as regards one or more of the foregoing criteria. 20

20 Reactant emulsifiers or surfactants for use in the emulsion polymerization of various olefinic monomers including acrylates, acrylic acid, acrylonitrile, styrene, butadiene, and vinyl acetate, to produce homo- and copolymer products, graft, and block polymers and the like are described, for example, in U.S. Patent 4,224,455. The emulsion polymer products are described as being useful for paper coatings, and paints and are characterised as having adhesion and scrub resistance. The emulsifiers which are described comprise the sulphonated half ester reaction products of maleic anhydride and an alkoxylated arylol containing nuclearly substituted alkyl. 25

25 In accordance with the present invention it has been discovered that stable, low floc latices having good shear characteristics and useful as pressure and non-pressure sensitive adhesives can be prepared via an emulsion polymerization process utilizing non-sulphonated monomeric emulsion stabilizer compounds which are half-esters of α, β -ethylenically unsaturated dicarboxylic acids or anhydrides, or mixtures thereof. 30

30 The present invention aims to provide stabilizer compounds, and emulsion polymerization processes using such stabilizers, as well as the resultant latex polymerizes wherein the foregoing problems are eliminated or at least mitigated substantially. 35

35 The invention also aims to provide stabilizer compounds effective for use in the emulsion polymerization of acrylate monomers generally to provide stable, low floc latices having good shear and chemical stability and improved water vapour transmission rates. 40

40 The invention further aims to provide stabilizers for use in emulsion polymerization which permit the use of polymerization catalysts which are electrolytes, without appreciable adverse effect. 45

45 The invention also aims to provide stabilizers for such use free or substantially free of any tendency to deleteriously effect or functionally impair latex products prepared for adhesive use. The invention also aims to provide latex products having utility as adhesives in diverse industrial applications. 50

50 According to the broader aspects of the present invention there are provided stabilizers for the emulsion polymerization of α -mono-ethylenically unsaturated monomer systems comprising acrylic type monomers, e.g. acrylates or acrylonitrile; vinyl type monomers e.g. vinyl chloride, vinyl acetate or vinylidene chloride; or styrene, the stabilizer being the half esters of α -ethylenically unsaturated dicarboxylic acids (or anhydrides) with non-ionic hydroxyl-containing surfactants. The preferred dicarboxylic acids (or anhydrides) are represented by maleic acid, itaconic acid, citraconic acid and glutaconic acid but generally any dicarboxylic acid containing at least one olefinic bond copolymerizable with an acrylic or vinyl moiety can be employed. It is preferred that the olefinic bond be adjacent to one of the carboxyl groups and it is most preferred that the olefinic linkage be adjacent to both carboxyl groups as in maleic and citraconic acids. Although in itaconic acid the olefinic linkage is not adjacent to both carboxyl groups it is one of the most preferred species, as well, since itaconic acid contains a reactive vinyl group adjacent one carboxyl group. Generally, the dicarboxylic acids should contain from 2 to 10 carbon atoms and preferably 2 to 4 carbon atoms in addition to the two carboxylic carbon atoms. 55

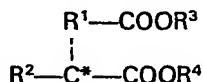
55 The non-ionic reactant generally has the formula

66 $R = (CH_2CH_3O)_x \dots$ will be the etheroxy chain by an oxygen, nitrogen or

wherein R represents a hydrophobe moiety linked to the ethenoxy chain by an oxygen, nitrogen or sulphur atom (chalcogen) and x is an integer of from 4 to 10. The preferred hydrophobe precursors are C_8 to C_{30} alcohols and phenols and more preferably they are C_{10} to C_{20} aliphatic alcohols or alkylated

phenols containing from one to three and preferably one or two alkyl groups of C₄ to C₁₈ and preferably C₄ to C₉, e.g. diisobutyl phenol, nonyl phenol, and dinonyl phenol.

A general formula for the esters of the present invention is as follows:



5 wherein R¹ represents a CH group; a CH₂=C group; or a (C₁ to C₃ alkyl)-C group; 5
 R² represents a hydrogen atom or C₁ to C₄ alkyl group;

R³ and R⁴ each represent M or -(OCH₂CH₂)_xR⁵; and wherein one of R³ and R⁴ is M and the other is -(CH₂CH₂O)_xR₅; and M represents a hydrogen atom or a salt forming group (e.g. an alkali metal atom, or an ammonium or amine group);

10 R⁵ represents a hydrophobic moiety (including the chalcogen atom) of the non-ionic reactant 10
 described above; x has a value of from 4 to 10; and when R¹ represents a CH group; or a (C₁ to C₄-alkyl)-C group, then the R¹-C* linkage is an olefinic double bond.

According to a further aspect of the invention there is provided a process for preparing the stabilizer compounds.

15 In yet a further aspect of the invention there is provided a process for the emulsion polymerization 15
 of such monomer systems comprising contacting, preferably at 50 to 70°C (but not limited thereto), in an aqueous pH medium of 4 to 6 (depending on the monomers employed), the aforescribed monomers and stabilizer in the presence of an effective amount of polymerization catalyst to form a stable latex having about 45 to 55% solids, the weight ratio of monomer to stabilizer being from about

20 50:1 to 10:1, the ratio of the said monomer to stabilizer being from about 50:1 to 10:1, the said monomer stabilizer and catalyst being added to the said aqueous medium in the form of an aqueous pre-emulsion, a first portion thereof, consisting of up to about 20% of the total amount of the said pre-emulsion, being initially added, the remainder thereof being added when the polymerization reaction 20
 has attained an initial exotherm, the said temperature and pH being maintained throughout the polymerization reaction. 25

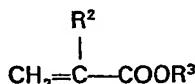
In a still further aspect of the invention there is provided stable latex products having a good adhesion property permitting their effective use as pressure sensitive adhesives, or binder adhesive latices or the like having diverse industrial applications.

30 The stabilizer compounds are best prepared by the reaction of the α -unsaturated acid (or anhydride) with a nonionic emulsifier of the formula R-CH₂CH₂O_xOH, wherein R and x have the aforesigned significance, in a solvent-free bulk system at a temperature of from about 80 to 120°C 30
 wherein the mole ratio of ionic emulsifier to acid or anhydride is about 0.5:1 to 1:1. At least substantial conversion of reactants to the half ester can be achieved on production scales in periods ranging from about 5 to 8 hours.

35 Suitable nonionic emulsifier reactants for forming the half esters include (and are exemplified by) the following commercially available materials: TRITON X-45 supplied by Rohm and Haas comprising 35
 octyl phenol containing a pentaethoxy group (hereinafter designated EOP-5); IGEPAL CO-530 supplied by GAF comprising nonyl phenol containing a hexaethoxy group (hereinafter designated ENP-6); IGEPAL CO-630 supplied by GAF comprising nonyl phenol containing a nonaethoxy group 40
 (hereinafter designated ENP-9); TERGITOL NP-14 supplied by Union Carbide comprising nonyl phenol containing a tetraethoxy group (hereinafter designated ENP-4), and TERGITOL 15-S-5 supplied by Union Carbide comprising linear C₁₁-C₁₅ alcohol containing a pentaethoxy group (hereinafter designated ELA-5).

45 The stabilizers herein may be characterized as ethoxylated monomeric emulsion stabilizers, i.e. EMES, the term monomeric being appropriate since, as will be explained, substantial portions thereof participate via activation of their olefinic double bond in the propagation of the polymer chain during emulsion polymerization of the acrylic monomer system. The affected EMES compound apparently becomes included mer unit in the polymer chain or otherwise associates with the polymer through a stable bonding mechanism. This conclusion is supported on the basis of liquid chromatography analysis 45
 of the resultant latex.

50 The stabilizing and other beneficial effects attributable to the EMES are manifest generally with respect to the emulsion polymerization of diverse types of acrylic monomers including mixture thereof with copolymerizable polar monomers containing a single double bond, i.e. α,β -mono-olefinic unsaturation. Acrylic monomers can be represented as follows:



55 wherein R² represents a hydrogen atom or a methyl group and R³ represents an alkyl group of 1 to 14 and preferably 1 to 8 carbons. Should R³ be in the higher range e.g. 8 and above, it is recommended 55

wherein R² represents a hydrogen atom or a methyl group and R³ represents an alkyl group of 1 to 14 and preferably 1 to 8 carbons. Should R³ be in the higher range e.g. 8 and above, it is recommended

that at least 2 to about 20% of the selected acrylic monomer have an R^3 group in which the number of carbon atoms is less than 4 to enhance cohesive strength of the resultant polymer. Acrylic monomer species include for example, 2-ethylhexyl acrylate (2-EHA); butyl acrylate (BuA); methyl methacrylate (MMA); and ethyl acrylate (EA). Polar monomers copolymerizable therewith having reference to the 5 conditions employed in the emulsion polymerization process include, for example, acrylic acid (AA), methacrylic acid (MAA), vinyl acetate (VA), acrylonitrile (AN), N,N-dimethylacrylamide (NNDMA), the reaction product of hydroxypropyl acrylate and succinic anhydride (HPASA) and the like. In forming the product latex, the acrylic monomer species may be used singly or in admixture with other acrylic or polar comonomers or mixtures thereof. The choice of monomer necessarily has reference to the use to 10 which the end product is to be put. With respect to adhesives, monomers are selected which typically form tacky, adhesive polymerizes, supplemented if advisable, by monomer(s) e.g. styrene, methyl acrylate, methyl methacrylate, which impart cohesive strength to the latex product. This is particularly important when preparing pressure sensitive adhesives. In the latter case, it is beneficial to employ, for example, major proportions of 2-ethylhexyl acrylate, preferably in amounts constituting at least about 15 65% by weight of the total acrylic and polar monomer, charged to the polymerization reactor. Mixtures of the 2-ethylhexyl acrylate with up to about, for example, 20% butyl acrylate, and 5% methyl methacrylate or 5% N,N-dimethylacrylamide or a mixture thereof are particularly effective for forming latices having pressure sensitive adhesive utility, e.g. when coated on vinyl and Dexter papers. 10

Other useful monomers include vinyl chloride, vinylidene chloride, conjugated dienes such as 20 butadiene-1,3; and vinyl-substituted aromatics e.g. styrene. In this regard particularly effective non-pressure monomer systems include butadiene alone or with styrene or acrylonitrile or mixtures thereof. The latter butadiene systems may be rendered pressure-sensitive by mixing with suitable tackifiers well known in the art such as terpene resins and rosin ester resins as well as those of the polymeric type based upon polymers of α -methyl styrene, vinyl toluene, and styrene and other compounds also known 25 to the art. 25

Similarly, by suitable choice of monomer as well as EMES compound, polymer adhesive latices of the non-pressure sensitive type may be provided as will be later explained in detail. In these cases ethyl acrylate replaces 2-ethylhexyl acrylate as the primary monomer and is effectively used in combination with relatively large amounts of methyl methacrylate e.g. up to about 30% based on total monomer 30 charge. 30

The EMES stabilizers provide significant advantages from both the process and product standpoints when used in amounts ranging from about 2—10 phm (parts per hundred parts of monomer) with a range of 2.5 to 6 phm being preferred. Polymer latex yields corresponding to 90% and higher conversions of monomer reactants are attainable. The need for surfactant emulsifants is 35 eliminated, and accordingly, the water sensitivity and surfactant migratory problems normally encountered therewith are avoided. The polymer latices characteristically display good shear and chemical stability with little or no tendency to undergo phase separation or coagulation despite prolonged standing. The latex is able to tolerate significant quantities of electrolyte without coagulating enabling the use of persulphate type free radical polymerization catalysts. Floc is eliminated or at least 40 reduced to negligible levels provided the pH levels are maintained within the range herein prescribed. However, choice of monomer may permit slight deviations. The latices obtained have relatively high solids content on the order of 45—55% and in the case of adhesives, are not adversely affected or functionally impaired by the presence of the EMES or other adjuvants recommended for use. Water vapour transmission rates (WVTR) are improved, compared to other stabilized polymer forming 45 emulsion systems thereby enhancing the utility of adhesive type polymer latices. As will be appreciated, the EMES can be used to advantage in acrylic emulsions generally to improve the chemical stability, shear and the like of the resultant latex regardless of the particular use contemplated for the product. 45

Additional polymerization catalysts preferred herein include peroxide type free radical initiators such as tertiary butyl hydroperoxide (90% solution), (TBHP) preferably in combination with sodium 50 formaldehyde sulphoxylate/ferrous ammonium sulphate, or alkali metal persulphates e.g. potassium persulphate, preferably in combination with a bisulphate solution such as sodium bisulphate. Catalyst amounts need only be those effective to initiate polymerization and are well known in the art. Choice of catalyst has regard also to the type of monomer(s) and reaction temperature in order to achieve maximum benefit. 55

To minimize if not eliminate flocculation, coagulation and the like, the pH of the polymerization reaction medium must be maintained at a value of at least about 4.5 and more preferably from about 5 to 7 in the case of hydrolyzable monomer(s). With certain monomers, pH values as low as about 4.2 are permitted. (Example 38 herein). As presently used, the term pH 4.5 aqueous medium is to be accorded a significance consistent with the foregoing. Adjustments in pH are made with a suitable base such as 60 ammonium hydroxide. 60

Polymerization reaction temperatures are usually maintained at about 50—80°C, selected values having reference to monomer, catalyst and EMES. Generally, peroxide-initiated polymerizations are carried out at 55—60°C whereas with persulphate catalysts, temperatures of 60—65°C are recommended. Generally, more broadly temperatures may range from about 0°C to about 100°C with 65 suitable known catalysts. 65

Optional ingredients to achieve particular effects may be included in the polymer-forming composition. Auxiliary dispersants, for example, may be used in small quantities of from about 0.3 to 0.8 phm as aids in reducing coagulum levels and/or viscosity. Particularly useful here is DAXAD 11, a product of the Dewey and Almy, Division of W. R Grace Co., comprising the sulphonated reaction product of formaldehyde and naphthalene.

The use of thickening agents to increase latex viscosity may be desirable where adhesive utility is contemplated. Examples of materials useful for this purpose include ACRYSOL ASE 95 (Rohm and Haas) and 68-710 (Reichold Chemicals, Inc.).

In carrying out the polymerization process, an aqueous pre-emulsion of the total charge of

10 monomer catalyst and EMES is formed with about 30-50 phm water. Auxiliary catalyst components such as the bisulphite and/or sulphoxylate/ferrous ammonium sulphate are excluded in the pre-emulsion being separately added as aqueous solutions. From 10 to 20% of the pre-emulsion is added to the reaction vessel along with additional water, usually from about 40-60 phm, and auxiliary dispersant, e.g. DAXAD-11. The total charge is heated to 50-70°C accompanied by a nitrogen flush. The

15 polymer-forming reaction ensues with the addition of 10 to 20% of the co-catalyst solution and after the initial exotherm subsides, the remaining pre-emulsion is added, preferably continuously over the remaining period for latex formation, usually 1½ to 2 hours. Along with the co-catalyst solution, the temperature of the reaction medium is maintained within the range stated, preferably 50-55°C, throughout the process, pH levels being maintained at 4.5 by addition of NH₄OH.

20 The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples. Examples 1 to 10 and 49 to 50 illustrate production of EMES and Examples 11 to 50 illustrate both peroxide and persulphate initiated polymerization in accordance with the invention. Parts are by weight.

EXAMPLES 1 TO 10

25 Examples of syntheses of EMES compounds in terms of reaction conditions and actual and theoretical, product yields are summarized in the following table. Syntheses were based upon an equimolar ratio of nonionic emulsifier and maleic anhydride except for Examples 1-4 in which a 0.57:1 nonionic to anhydride ratio was used. Although illustrated with respect to maleic anhydride other anhydrides of the types previously described may be used with equivalent results.

TABLE I

Ex. No.	Nonionic Emulsifier	Reaction Time (hours)	Temp. °C	Product yield litre meq/g Theoretical	Found
1	ENP-9	5	80-100	3.17	2.67
2	ENP-9	7	90	3.17	2.77
3	ENP-9	6.5	118	3.17	3.53
4	ENP-9	8	100	3.17	3.00
5	ENP-9	7	100	1.40	1.72
6	ENP-4	7	80	2.02	1.96
7	EOP-5	7	100	1.91	1.63
8	ELA-5	6	95-100	1.93	1.83
9	ELA-5	7	95-105	1.93	2.02
10	ENP-6	7	95-100	1.72	1.84

In all cases, product yield corresponds to at least about 80% conversion of reactants and in most cases, at least about 90%. Instances where "found" titre values exceed theoretical are probably explained by the stoichiometry of the reactants in that the molecular weight of the nonionic reactant is based upon a published average value and may thus be inexact in a specific case.

EXAMPLE 11

The following composition was prepared:

		Parts
5	2 EHA (2-ethylhexylacrylate)	80
	BuA (butyl acrylate)	13
	AA (acrylic acid)	2
	EMES of Example 2	5
10	H ₂ O	100
	DAXAD 11	0.5
10	Fe(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O	0.00136
	SFS (sodium formaldehyde sulphonylate)	0.12
	TBHP (90% solution) (tertiary butyl hydroperoxide)	0.18

Monomer, EMES and TBHP were pre-emulsified in 35 parts water. The reactor was charged with 15 50 parts water, DAXAD 11 and 10% of the pre-emulsion, the latter by addition funnel. The 15 sulphoxylate/ferrous ammonium sulphate in 15 parts water was added by another addition funnel. The charge was heated to 50°C accompanied by N₂ flush and 10% of the sulphoxylate/ferrous ammonium sulphate was added. After the initial exotherm, the remaining pre-emulsion and co-catalyst solution was 20 added continuously for about 1½ hours maintaining a temperature of 50—55°C throughout the process. 20

EXAMPLE 12

Example 11 was repeated using the following monomer system:

		Parts
25	2 EHA	80
	Bua	10
	AA	5

EXAMPLE 13

Example 12 was repeated with the following modifications:

K₂S₂O₈ was used as the catalyst (0.3 part) and was prepared as a pre-emulsion with monomer 30 and EMES in 47 parts water. Polymerization was effected by heating the initial reactor charge of pre-emulsion (10% of total) and DAXAD 11 to 55—60°C with N₂ flush and adding NaHSO₃, (0.075 part in 3 parts water). The procedure was otherwise as explained in Example 12. 30

In each of Examples 11—13, a stable latex of about 50% solids was obtained having the characteristics summarized in Table 2.

TABLE 2

Example No.	% Free Stabilizer	Latex pH	Floc	Conversion
11	2.0	6.8	0.5	99+
12	1.8	7.1	nil	97
13	—	5.0	nil	95

5 The results indicate practically total conversion of monomer and the virtual absence of floc for both peroxide and persulphate initiated systems. This illustrates the capacity of the present compositons to tolerate electrolyte with little or no adverse effects. As determined by liquid chromatography, about 60% of the EMES was incorporated into the polymer latex product of these examples. 5

EXAMPLE 11B

10 When Example 11 was repeated at pH 2 in the reaction medium, total flocculation occurred. The effects of varying the EMES compound with respect to a given monomer system are summarized in Examples 14—22. 10

EXAMPLES 14—22

Example 11 was repeated using the following monomer system:

			Parts
15	2 EHA		75
	BuA		15
	AA		5

EMES, 5 parts, was used as indicated in the following Table:

TABLE 3

Ex. No.	EMES From Ex. No.	% Conversion	% Floc	Latex pH	% Solids	Brookfield Viscosity (RVT) cps
14	2	97.7	nil	4.9	48.5	1,100 ^a
15	2	99.5	nil	6.2	49.3	2,650 ^a
16	6	99.9	1.6	5.6	44.4	12,200 ^b
17	8	98.6	nil	6.3	49.3	3,500 ^b
18	10	96.0	nil	6.0	48.0	7,200 ^b
19	9	100	nil	5.7	50.0	4,120 ^b
20 ^d	9	94.0	1.5	6.2	49.0	3,165 ^c
21	5	95.4	0.5	6.8	47.6	9,280 ^b
22	7	95.0	nil	5.8	47.5	—

Notes on Table 3

- a) #3 spindle @ 20 RPM
- b) #5 spindle @ 20 RPM
- c) #2 spindle @ 20 RPM
- d) DAXAD 11 omitted

5

5

It should be noted that a floc-free latex was obtained in Example 14 despite a pH of slightly less than 5. Increasing the pH to 6.2 and using the same EMES (Example 15) leads to improved conversion (99.5% vs. 97.7%) and increased solids (49.3% vs. 48.5%) and viscosity (2,650 vs. 1,100). However, when Example 14 was repeated at pH 4.4, floc increased to 39%. This comparative data again shows the importance of maintaining the prescribed pH levels to minimize coagulum formation. This can largely be explained by the fact that the EMES compounds become increasingly water insoluble below about pH 5 and thus relatively unstable polymerization systems may be expected. Omission of DAXAD 11 (Example 20) produced only a slight increase in floc (1.5% vs. nil). The relatively high latex viscosities are probably due, at least in part, to the high AA content and latex particle sizes.

10 The use of varying amounts of DAXAD 11 at recommended pH and low EMES levels is summarized in Examples 23—28.

15

EXAMPLES 23—28

Example 11 was repeated with monomer composition and DAXAD 11 concentration modified as indicated in the following Table 4. In each case, the EMES of Example 9 was used.

TABLE 4

Ex. No.	Parts		Monomer		EMES		pH	% Floc
	Daxad 11	2 EMA	BuA	AA	parts			
23	0.5	75	19	5	1	8.6	10.7	
24	0.5	75	18	5	2	8.4	nil	
25	0	75	18	5	2	8.3	4.0	
26	0	74	18	5	3	8.1	1.5	
27	0.5	75.5	15.5	5	4	6.8	nil	
28 ^a	0.5	75.5	15.5	5	4	5.5	nil	

Note on Table 4

^a 10 gallon reactor run.

In each of Examples 23—26, a latex polymerizate was obtained; however, complete coagulation occurred in each case within one week. Nevertheless, the effect of DAXAD 11 on flocculation should be noted. Thus at 1 part EMES (Example 23), DAXAD 11 apparently had little effect (10.7% floc). However, 25 omitting DAXAD 11 (Example 25) from an otherwise identical composition (Example 24 0.5 part DAXAD 11) containing but 2 parts EMES increased floc from nil to 4.0%. At recommended EMES levels of 4 parts (Examples 27 and 28), stable, floc-free latices were obtained. The 10 gallon reactor run of Example 28 differs from Example 27 primarily in the latex viscosity, the measured values being 69 and 4400 respectively. The discrepancy is thought to be due to a difference in the particle size or to a pH effect or both. So far as percent conversion and solids content is concerned Examples 27 and 28 are closely similar to the previous examples.

30

The latices obtained in Examples 11—22 and 27—28 are useful as pressure sensitive adhesives. 35 The cohesive strength of these products can be increased, for example, by the use of methyl methacrylate in the monomer composition. This is illustrated in Examples 29—34.

EXAMPLES 29—34

Example 11 was repeated except for the inclusion of MMA in the monomer composition as indicated in the following Table 5. In each case, the EMES of Example 9 was used at 5 parts.

TABLE 5

Ex. No.	Monomer				% Floc	% Solids	% Con- ver- sion	pH	Brookfield Viscosity #5 Spindle @ 20 RPM
	2 EHA	BuA	MMA	AA					
29	75	12.5	2.5	5	nil	48.3	96.6	6.6	5920
30	72.5	15	2.5	5	nil	48.8	97.6	6.6	5800
31	75	10	5	5	nil	48.8	97.6	6.6	2120
32	70	15	5	5	nil	49.0	98.0	6.6	9000
33 ^a	75	12.5	2.5	5	nil	51.4	100	8.8	—
34 ^a	70	15	5	5	nil	51.0	100	8.1	—

Note on Table 5

a) 10 gallon reactor run.

5 In each case, a stable latex having good cohesive strength was obtained.

The previous examples illustrate monomer systems based on 2-ethylhexyl acrylate, butyl acrylate and acrylic acid. In the following Examples, one or more monomers are included therewith or one or both of the butyl acrylate and acrylic acid monomers is replaced as indicated. 5

EXAMPLES 35—39

10 Latices obtained for modified monomer systems were evaluated and the results reported in Table 6 below. 10

The EMES of Example 2 was used in each example.

TABLE 6
Latex Analysis: pH—% Floc—% Conversion

Example No.	35 ^a	36 ^a	37 ^b	38 ^b	39 ^b
EMES content	7.5 parts	10 parts	5 parts	4.8 parts	5 parts
	pH-Floc-Conv.	pH-Floc-Conv.	pH-Floc-Conv.	pH-Floc-Conv.	pH-Floc-Conv.
					7.6-nil-94
					7.0-nil-96
					4.9-nil-99+
					4.2-nil-
					4.3-5.0-92.5
Composition	Monomer Content				
2 EHA	80	80	80	76.2	80
BuA	15	10	10	9.5	—
HPA-SA ^c	5	10	10	—	—
AA	—	—	—	4.8	5
NNDMA ^b	—	—	—	4.8	—
VA	—	—	—	—	10
EA	—	—	—	—	—
AN	—	—	—	—	—

Notes on Table 6

a) peroxide initiated polymerization method of Example 11
 b) persulphate initiated polymerization method of Example 13
 c) reaction product of hydroxy propyl acrylate and succinic anhydride
 5 d) N,N-dimethyl acrylamide

In Example 38, despite a pH of 4.2 "nil" floc is reported indicating that the type of monomer system used is relevant in establishing pH limits. This is to be compared with Example 16 wherein floc increased from 1.6 to 39% for a corresponding pH change of 5.6 to 4.4. In the two examples 16 and 38 it should however be noted that tested catalyst, EMES and monomer composition differed. One can also 10 compare Example 39 indicating a floc level of 5% at pH 4.3. It is to be observed that Examples 38 and 39 are based on persulphate initiated polymerization. The product latices were stable and otherwise favourably characterised in accordance with the criteria hereinbefore defined. 10

The adhesion properties of various of the afore-described latices were evaluated by coating (hand casting) vinyl film and Dexterpaper from the respective latices. Reactor synthesized samples were cast 15 onto vinyl film on the spread line from emulsion. Test results are summarized in Table 7. 15

TABLE 7A
 Pressure Sensitive Adhesion Properties
 Vinyl Base

Latex of Ex. No.	Thickness Mils	Tack	Probe Tack g.	Adhesion Steel (oz/in)	Adhesion Backing (oz/in)	Quick Stick (oz/in)	T—Peel (oz/in)
14	0.8	4.6	358	17	—	10	10
16	1.8	5.2	300	19	17	14	15
17	1.1	5.0	446	18	15	17	13
18	1.6	6.1	436	22	18	19	12
20	1.3	5.4	448	21	15	17	10
21	1.4	4.9	314	17	9	15	10
22	1.4	3.1	388	26	23	22	17
27	1.0	5.7	374	13	12	11	8
27 ^a	1.4	5.6	368	10	9	10	6
29	1.4	5.8	368	41	16	14	—
29 ^a	1.6	5.2	298	18	18	14	14
30	1.3	5.2	324	18	18	12	—
31	1.0	6.0	348	20	19	15	—
32	1.5	5.2	236	19	15	12	—
32 ^a	1.5	4.9	314	17	19	15	11

TABLE 7B
Dexter Paper Base

Ex. No.	Mass. wgt. g/yd ²	WVTR	^b Porosity in/5 min.
14	37.9	59.4	—
16	37.8	109	0.39
17	34.0	67.8	0.7
18	52.6	60	0.23
20	32.3	120	1.08
21	35.3	71.5	0.03
22	39.2	104	1.48
27	41.1	77.5	0.25
27 ^a	42.5	83.5	0.53
29	41.0	77.4	0.08
30	38.2	76.1	0.11
31	39.1	80	0.38
32	53.9	55.7	0.04
32 ^a	57.3	55.7	0.21

Notes on Table 7A and 7B

a) 10 gallon reactor batch
b) heavy cylinder

5 Testing of the foregoing samples is in accordance with standardized techniques well known in the art. Porosity was measured with the Gurley Instrument using the heavy cylinder. The standard test was modified due to the relatively non-porous nature of the coated paper. After release of the cylinder, the cylinder movement in inches was measured over a 5 minute period. In most cases, the cylinder failed to reach the zero calibration mark, usually signifying non-porous. The latex of Example 16 exhibited a 5 marked increase in WVTR, 109 g/100 in²/24 hr. This essentially duplicated earlier results obtained with a 2EHA/BuA/AA/EMES (Example 6) (80/13/2/5) copolymer in which the measured WVTR was found to be 83 g/100 in²/24 hr. The WVTR data is somewhat erratic and of course is dependent upon the porosity of the coated paper. The samples were for the most part found to be non porous. 10

10 The data perhaps suggests that the 4 mole and possibly the 5 mole ethoxyl EMES structures are more efficient in transporting water vapour. Assuming the same degree of incorporation of the EMES in the polymer, the data indicates that a distribution along the polymer chain of "short" ethoxy units appears to be more efficient than the "longer" ethoxy units in transporting water vapour. 15

15 A sample of the Dexter paper coated with the latex of Example 17 was evaluated for water transport by placing H₂O, containing some red dye, onto the adhesive surface. The sample was supported on the rim of a beaker during the test period. It was found that within 15—20 min. the H₂O was transported through the sample with the paper fibres dyed heaviest in the transport pattern. The area of greatest colour was then evaluated for permeability using the air densitometer with the heavy cylinder. No air transport was observed in 5 minutes indicating a non permeable (to air) product. This was found despite the relatively low WVTR (67.8) value determined for this sample. It is possible that 20 fibres extending above or out of the adhesive layer are able to conduct the water through the tape via a capillary action. Since the coatings are prepared directly from casting of the latex directly onto the Dexter paper it would not be expected to have any uncoated fibres on the surface. 25

20 Table 7 indicates the adhesion properties of the various 2EHA/BuA/MMA/AA/EMES copolymers to be essentially equivalent and independent of the EMES employed. In addition, the inclusion of MMA into the monomer feed at levels up to 5 parts did not appear to alter the adhesion properties. 30

The inclusion of MMA was found to improve the cohesive strength of the polymer, at a constant catalyst concentration and thus perhaps molecular weight.

It is apparent from the data that the elimination of Daxad 11 from the polymerization recip (Example 20) had no effect on the physical properties of the polymer structure under evaluation. The 5 increase in the WVTR of this sample in comparison to Example 17 is perhaps related more to the increased porosity than to the absence of the Daxad. If an effect would be expected on WVTR, it would be expected to increase with the presence of Daxad due to its complete water solubility.

Initial adhesion to skin including quick stick was found to be excellent for all the various polymers listed in Table 7.

10 The production of non-pressure sensitive adhesive latices is illustrated by the following examples 40 to 48 in which the monomer composition comprises ethyl acrylate (68 parts), methyl methacrylate (28 parts) and acrylic acid (4 parts).

15 The catalyst and polymerization procedure was that of Example 11. In each case, the resultant latex was found to be useful as the binder adhesive in the manufacture of a gypsum duct tape. The 10 results are summarized in Table 8.

TABLE 8
Binder/Adhesive Latices

Ex. No.	EMES Ex. No.	EMES parts	DAXAD 11 pHm	% Floc	pH	% Solids	% Con- ver- sion	Brookfield Viscosity #2 Spindle @ 20 RPM
40	9	5	0.5	nil	6.2	49.8	97.1	105
41	10	5	0.5	nil	6.5	49.7	96.9	—
42	2	5	0.5	2.6	6.1	49.5	99.1	—
43	5	5	0.5	nil	6.1	50.0	97.5	—
44 ^a	5	5	0.5	nil	6.1	50.2	97.8	560
45 ^a	2	2.5	—	nil	6.7	51.4	100	50
46 ^a	2	2.5	—	2.0	6.5	49.8	99.1	46
47	5	2.5	—	nil	6.9	50.5	98.4	116
48 ^a	5	2.5	—	nil	6.2	49.1	95.7	57

Note on Table 8

a) 10 gallon reactor batch.

20 Compared with the pressure sensitive adhesive discussed earlier, the latex viscosities of Examples 41—49 were lower by orders of magnitude 50 vs. 1,000. Exceptionally clean polymerization was obtained for Examples 40, 41, 43, 44, 47, and 49. The latices of Examples 43, 46 and 47 exhibited floc levels of 0 to 3% and are considered to be of borderline stability.

25 The latices of Examples 40—49 were evaluated for the dual purpose as binder for a cloth impregnated gypsum tape product and as the structural adhesive for use in its application to sheet metal ducts.

A. Gypsum Tape Adhesive

30 Each of the tested latices was found to be non tacky and depending upon the EMES employed, produced the desired structural bond of the tape to the galvanized sheet metal. The Examples 40 and 41 latices stabilized with the materials of Examples 9 and 10 did not appear to produce the desired bond. Polymers stabilized with the materials of Examples 2 and 5 were found to produce the desired bond. In order to achieve a reproducible bond it was found necessary to thicken the latex to approximately 1500 cps with Acrysol ASE95 or other thickening agents well known in the art. With thickening, the rheology of the latex was apparently sufficiently altered that the absorption of the latex by the gypsum was inhibited and therefore the latex remained at the interface.

35 With respect to Examples 40 and 41, it is apparent that the distribution and perhaps concentration of ethoxy functionality along the chain of the EMES is of importance. Apparently, the greater the polyethoxy unit chain length, the less the molar quantities of the EMES in the polymer structure,

assuming the same concentration in the polymerization reaction. Moreover, the hydrophilicity of the EMES compound increased with increasing ethoxy chain length.

The latices of Examples 42—48 were found to waterproof the gypsum tape and stabilize medical plaster casts when immersed in water. The latices of Examples 44, 45 and 47 gave excellent slurry and 5 coating stability without the need of further additives and facilitated the inter-binding of gypsum particles as well as the binding of such particles to a cotton backing thus providing a flexible gypsum impregnated tape product.

A typical formulation for such utility is as follows:

		Weight %	
10	Plaster (Gypsum)	26.3%	10
	H ₂ O	65.7	
	EMES Structured Latex	8.0	

Further testing of these compositions suggests their utility as non-woven binders.

EXAMPLE 49

15 Examples 1 to 10 were each repeated (Examples 49a to 49j) using itaconic acid.

15

EXAMPLE 50

Examples 1 to 10 were each repeated (Examples 50a to 50j) using citraconic acid.

CLAIMS

20 1. A monomeric polymerisable monoester of an ethylenically unsaturated dicarboxylic acid with a non-ionic ethoxylate of the formula

20



wherein R represents a C₈—₃₀ linear alkyl group or a C₄—₁₈ mono-, di-, or tri-alkylated phenyl group and the R group is linked to the ethenoxy group by an oxygen, nitrogen, or sulphur atom and wherein x has a value of from 4 to 10.

25 2. A stabilizer as claimed in Claim 1 in which R represents a p-octyl- or p-nonyl-phenyl group.

3. A stabilizer as claimed in Claim 1 in which R represents a linear alkyl group of 11 to 15 carbon atoms and x is 5.

4. A stabilizer as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples 1 to 10, 49 or 50.

25

30 5. A process for the emulsion polymerization of one or more acrylate monomers alone or in admixture with one or more copolymerizable polar monomers of the vinyl or acrylic type comprising contacting the said monomers with a stabilizer as claimed in any one of Claims 1 to 4 and an effective amount of polymerization catalyst at a temperature of about 5—80°C in an aqueous medium having a pH above about 4 to form a stable product latex of 45 to 55% solids, the weight ratio of monomer to stabilizer being from about 50:1 to 10:1, the said monomer, stabilizer and catalyst being added to the said aqueous medium in the form of an aqueous pre-emulsion, a first portion thereof constituting up to about 20% by weight of the total pre-emulsion to be charged being initially added, the remainder thereof being added when the polymerization reaction has attained an initial exotherm, the said temperature and pH being maintained throughout the latex forming polymerization reaction.

30

40 6. A process as claimed in Claim 5 in which the pH is from about 4 to 8.

7. A process as claimed in Claim 5 or Claim 6 in which the said catalyst is t-butyl hydroperoxide.

8. A process as claimed in Claim 5 or Claim 6 in which the said catalyst is potassium persulphate.

9. A process as claimed in Claim 5, 6, 7 or 8 in which the reaction mixture includes a small but effective amount of sulphoxylate/ferrous ammonium sulphate.

40

45 10. A process as claimed in any one of Claims 5 to 9 in which the reaction mixture includes a small but effective amount of sodium bisulphite.

11. A process as claimed in any one of Claims 5 to 10 in which the reaction mixture includes from 0.3 to 1.0 phm of a sulphonated reaction product of formaldehyde and naphthalene.

12. A process as claimed in any one of Claims 5 to 11 in which the said acrylate monomer

45

50 comprises at least about 65% by weight 2-ethylhexyl acrylate.

50

13. A process as claimed in any one of Claims 5 to 12 in which the acrylate monomer includes up to about 20% butyl acrylate and up to about 5% acrylic acid.

14. A process as claimed in any one of Claims 5 to 13 in which the acrylate monomer includes up to about 5% methyl methacrylate.

15. A process as claimed in any one of Claims 5 to 14 in which the reaction mixture includes up to about 10% vinyl acetate, 3% acrylonitrile, 15% ethyl acrylate, and 5% dimethyl acrylamide or 20% of the reaction product of hydroxyl propyl acrylate and succinic anhydride or a mixture thereof.

5 16. A process as claimed in any one of Claims 5 to 11 in which the said acrylate monomer comprises at least about 65% by weight ethyl acrylate. 5

17. A process as claimed in Claim 5 substantially as specifically described herein with reference to any one of Examples 11 to 48.

18. A latex whenever made by a process as claimed in any one of Claims 5 to 17.

10 19. A latex as claimed in Claim 18 in an aqueous, gypsum solution.

20. An adhesive comprising a latex as claimed in Claim 18 or Claim 19. 10

21. An adhesive element comprising a base coated with an adhesive as claimed in Claim 20.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1983. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.